

VAPOR-LIQUID EQUILIBRIA FOR THE BINARY MIXTURE OF PROPANE (R-290) + ISO-BUTANE (R-600A)

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Abstract

Isothermal vapor-liquid equilibria data for the binary mixture R-290/R-600a at four equally spaced temperatures between 273.15 and 303.15K were measured by using a circulation-type equilibrium apparatus. The experimental data were correlated with the Carnahan-Starling-De Santis equation of state and the Peng-Robinson one combined with the Wong-Sandler mixing rule. It was confirmed that the data calculated by these equations of state have a good agreement with experimental data. Azeotropic behavior was not found in this mixture.

Keywords: Hydrocarbon; Propane (R-290); Iso-butane (R-600a); CFC alternative refrigerant; Vapor-liquid equilibria (VLE); Carnahan-Starling-De Santis equation of state (CSD-EOS); Peng-Robinson equation of state (PR-EOS).

1. Introduction

Much effort has been made to find the suitable replacements for chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs) due to their high ozone depletion potentials (ODPs) and global warming potentials (GWPs). Hydrofluorocarbons (HFCs) - synthetic refrigerants having zero ODPs - were proposed as promising replacements for CFCs and HCFCs. Unfortunately, HFCs have been included in the basket of green house gases to be regulated by Kyoto Protocol. In recent years, the utilization of light hydrocarbons as effective refrigerants is believed as an alternative solution because these hydrocarbons are rather cheap, plentiful and environmentally benign chemicals (zero ODPs and near zero GWPs) and have many outstanding properties. Their flammability has caused some concerns but all tests done so far indicated that they are so quite safe in small applications such as domestic fridge and car air-conditioner [1]. In this work, isothermal vapor-liquid equilibria data for the binary mixture R-290/R-600a at four equally spaced temperatures between 273.15 and 303.15K were measured by using a circulation-type equilibrium apparatus. The experimental data were correlated with the Carnahan-Starling-De Santis equation of state (CSD-EOS) and the Peng-Robinson equation of state (PR-EOS) combined with the Wong-Sandler mixing rule. The interaction parameters and average deviations of pressures and vapor phase compositions obtained from these equations of state were presented.

2. Experimental

2.1. Chemicals

Propane (> 99.5% mass) supplied by MG Industries, U.S.A. and iso-butane (> 99.8% mass) supplied by Jeong Il Co., Korea were used in this work.

2.2. Vapor-liquid equilibrium apparatus

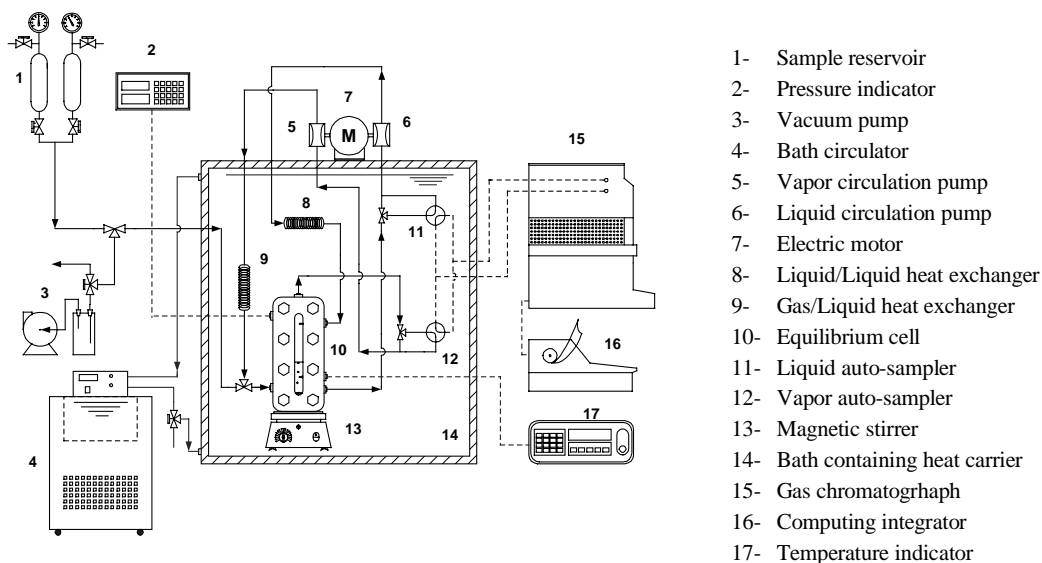


Figure 1. Schematic diagram of the vapor-liquid equilibrium apparatus

The schematic diagram of vapor-liquid equilibrium is illustrated in Figure 1. The equilibrium cell (10) is a 316 stainless steel with an inner volume of about 85ml. A pair of Pyrex glass windows was installed on two sides of the cell in order to make it possible to observe the inside during operation. Inside the cell, a stirring bar rotated at variable speeds by an external magnetic stirrer (13) is used to accelerate the attainment of the equilibrium state and to reduce concentration gradients in both phases. The temperature of the equilibrium cell in the bath (14) is maintained by constant temperature heat carrier circulated by using the bath circulator (4) (RCB-20 model manufactured by Jeio Tech, Korea). In case desired temperature of the cell was higher than 273.15K, water could be used as heat carrier in this bath. On the contrary, solution of methanol + water was recommended.

The temperature of the sample in the cell was measured with a platinum resistance sensor connected to a digital temperature indicator (17) - F250 precision thermometer model manufactured by Automatic Systems Laboratories Ltd., UK. They were calibrated by NAMAS accredited calibration laboratory. The total error in temperature measurements is estimated to be within $\pm 0.01\text{K}$. The pressure was measured with a model XPM60 pressure transducer and digital pressure calibrator indicator (2) - PC106 model manufactured by Beamax, Finland. Pressure calibrations are traceable to national standards (Center for Metrology and Accreditation Certificate Nos. M-95P077 dated 14-

11-1995, M-M730 dated 16-11-1995 and M-95P078 dated 16-11-1995). The total errors in pressure measurements were estimated to be within ± 0.001 MPa.

The vapor and liquid phases in the equilibrium cell were continuously re-circulated by a dual-head circulation pump (a product of the Milton Roy Company, USA.) including vapor circulation pump (5), liquid circulation pump (6) and electric motor (7). After equilibrium was reached, the vapor and liquid samples were withdrawn from the recycling loop and injected on-line into a Gow-Mac model 550P gas chromatograph (GC) by vapor and liquid auto-samplers (12 and 11). This GC was equipped with a thermal conductivity detector (TCD) and a Porapak Q column from Alltech Company. The signals from G.C were processed and converted to data by D520B computing integrator (16) supplied by Young In Co., Korea.

2.3. Experimental procedures

The system was firstly evacuated by vacuum pump (3) to make sure that all inert gases were removed. An adequate amount of R-600a contained in sample reservoir was introduced into the cell, and then the temperature of the entire system was maintained by controlling the temperature of the heat carrier in the bath (14). After desired temperature was achieved, the vapor pressure of the R-600a was measured.

After that, a desired amount of R-290 from reservoir was supplied into the cell. Both the dual-head pump and stirrer should be turned on continuously until the equilibrium state of the mixture in the cell was established. As soon as the equilibrium state was confirmed (after one hour at least), the compositions of the equilibrium-state sample as well as the pressure in the cell were measured. The GC was calibrated with pure components of known purity and with mixtures of known composition that were prepared gravimetrically. At least three analyses were performed for each phase and the average value was considered as corresponding to the equilibrium.

Finally, the vapor pressure of pure R-600a was measured in the same procedure mentioned above for R-290.

3. Correlation

In this work, the experimental VLE data were correlated with the CSD-EOS and the PR-EOS combined with the Wong-Sandler mixing rule.

3.1. The CSD-EOS

The CSD-EOS is expressed as follows

$$\frac{PV_M}{RT} = \frac{1 + y + y^2 - y^3}{(1 - y)^3} - \frac{a}{RT(V_M + b)} \quad (1)$$

$$\text{Where } y = \frac{b}{4V_M}, V_M: \text{molar volume} \quad (2)$$

In case of pure component, the temperature dependence of 'a' and 'b' are represented by the following forms:

$$a = \alpha_0 \exp(\alpha_1 T + \alpha_2 T^2) \quad (3)$$

$$b = \beta_0 + \beta_1 T + \beta_2 T^2 \quad (4)$$

The CSD-EOS using the approach of Morrison and McLinden [3] was adopted in correlating VLE data. The coefficients of α_0 , α_1 , α_2 in equation (3) and β_0 , β_1 , β_2 in equation (4) were cited from REFPROP 5.0.

In the application of CSD-EOS to mixture, there exists the effective molecular parameters a_m and b_m defined by using the following mixing rules:

$$a_m = \sum_{i=1}^n \sum_{j=1}^n x_i x_j a_{ij} \quad (5)$$

$$b_m = \sum_{i=1}^n \sum_{j=1}^n x_i x_j b_{ij} \quad (6)$$

where n is the number of components in mixture. When $i = j$, the values of a_{ii} and b_{ii} are those of 'a' and 'b' of the pure components which are determined by equation (3) and (4). The values of a_{ij} and b_{ij} can be obtained if nearly any experimental property of the mixture is known. For the binary systems, the values of a_{12} and b_{12} can be expressed as following forms:

$$a_{12} = (1 - f_{12}) (a_{11} a_{22})^{1/2} \quad (7)$$

$$b_{12} = \frac{1}{8} (b_1^{1/3} + b_2^{1/3})^3 \quad (8)$$

The mixing rule for the 'a' parameter for a mixture involves the interaction parameter, f_{12} , which must be determined from experimental data. The approach is to find the value of f_{12} , which minimizes the sum of square Γ of relative deviation between measured and calculated quantities:

$$\Gamma(T, x, f_{12}) = \omega_p \left(\frac{P_{\text{exp.}} - P_{\text{cal.}}}{P_{\text{exp.}}} \right)^2 + \omega_L \left(\frac{V_{L, \text{exp.}} - V_{L, \text{cal.}}}{V_{L, \text{exp.}}} \right)^2 + \omega_v \left(\frac{V_{v, \text{exp.}} - V_{v, \text{cal.}}}{V_{v, \text{exp.}}} \right)^2 + \omega_y (y_{\text{exp.}} - y_{\text{cal.}})^2 \quad (9)$$

Because the vapor composition must be between zero and unity, the last term in equation (9) is expressed as an absolute error. Moreover, the experimental data of vapor and liquid specific volume indicated in this equation are not available so the corresponding weighting factors in the expression of Γ are set to zero.

$$\Gamma(T, x, f_{12}) = \omega_p \left(\frac{P_{\text{exp.}} - P_{\text{cal.}}}{P_{\text{exp.}}} \right)^2 + \omega_y (y_{\text{exp.}} - y_{\text{cal.}})^2 \quad (10)$$

3.2. The PR-EOS

The Peng-Robinson equation of state [5] is expressed as follows:

$$P = \frac{RT}{V_M - b} - \frac{a(T)}{V_M(V_M + b) + b(V_M - b)} \quad (11)$$

$$a(T) = \left(0.457235 \frac{R^2 T_c^2}{P_c} \right) \alpha(T) \quad (12)$$

$$b = 0.077796 \cdot RT_c / P_c \quad (13)$$

$$\alpha(T) = \left[1 + k \left(1 - \sqrt{T/T_c} \right) \right]^2 \quad (14)$$

$$k = 0.37464 + 1.54226\omega - 0.26992\omega^2 \quad (15)$$

where the parameter ‘a’ is a function of temperature, ‘b’ is constant, k is a constant characteristic of each substance, ω is the acentric factor, P (MPa) is the pressure, P_c (MPa) is the critical pressure, T (K) is the absolute temperature, T_c (K) is the critical temperature, T_r is the reduced temperature, and V_M is the molar volume.

The Wong-Sandler mixing rule [6] was used in this work to obtain equation of state parameters for a mixture from those of the pure components. Wong and Sandler equated the excess Helmholtz free energy at infinite pressure from an equation of state to the excess Gibbs free energy from any activity coefficient model, in such a way that a mixing rule is obtained which simultaneously satisfies the quadratic composition dependence of the second virial coefficient but also behaves like an activity coefficient model at high density. This mixing rule for a cubic equation of state can be written

$$b_m = \frac{\sum_i \sum_j x_i x_j (b - a/RT)_{ij}}{\left(1 - A_\infty^E / CRT - \sum_i x_i a_i / RT b_i \right)} \quad (16)$$

$$\text{with } (b - a/RT)_{ij} = \frac{1}{2} \left[(b - a/RT)_i + (b - a/RT)_j \right] (1 - k_{ij}) \quad (17)$$

$$\text{and } \frac{a_m}{b_m} = \sum_i x_i \frac{a_i}{b_i} + \frac{A_\infty^E}{C} \quad (18)$$

where C is a constant equal to $\ln(\sqrt{2}-1)/\sqrt{2}$ for the PR-EOS used in this work, k_{ij} is binary interaction parameter. Also, A_∞^E is an excess Helmholtz free energy model at infinite pressure which can be equated to a low-pressure excess Gibbs free energy [7]; in this study we use the NRTL model [8] given by:

$$\frac{A_\infty^E}{RT} = \sum_i x_i \frac{\sum_j x_j G_{ji} \tau_{ji}}{\sum_r x_r G_{ri}} \quad (19)$$

$$\text{with } G_{ji} = \exp(-\alpha_{ji} \tau_{ji}) \quad \text{and} \quad \tau_{ji} = (g_{ji} - g_{ii}) / (RT) \quad (20)$$

where G_{ji} is the local composition factor for the NRTL model, τ_{ji} is the NRTL model binary interaction parameter, g_{ji} is an interaction energy parameter of the i-j component, α_{ji} is a nonrandomness parameter, and R is the universal gas constant. The critical properties (T_c , P_c) and acentric factors (ω) of R-290 and R-600a used to calculate the parameters for the PR-EOS are given in Table 1. We have set the non-randomness parameter, α_{ij} , equal to 0.3 for the binary mixture investigated here. The parameters of these equations were obtained by minimizing the following objective function:

$$\text{objective function} = \frac{1}{N} \sum_{i=1}^N \left[\left(\frac{P_{i,\text{exp}} - P_{i,\text{cal}}}{P_{i,\text{exp}}} \right) \times 100 \right]^2 \quad (21)$$

where N is the number of experimental points, P_{exp} is the experimental pressure, and P_{cal} is the calculated pressure.

Table 1. Characteristic properties of propane and iso-butane ^(a)

Characteristic property	Propane (R-290)	Iso-butane (R-600a)
Critical temperature, T_c (K)	369.85	407.85
Critical pressure, P_c (MPa)	4.248	3.640
Acentric factor, ω	0.1524	0.1853

(a) Source: database REFPROP 6.01 (1998) [4]

4. Results and discussion

The comparison of the saturated vapor pressure (P_v) of pure components between experimental data and data obtained from the database REFPROP 6.01 are shown in Table 2 where we can see that the absolute deviations of vapor pressure for both R-290 and R-600a were within ± 0.002 MPa and the average relative deviations ($\Delta P_v/P_v$) from database REFPROP 6.01 were 0.11% for R-290 and 0.51% for R-600a.

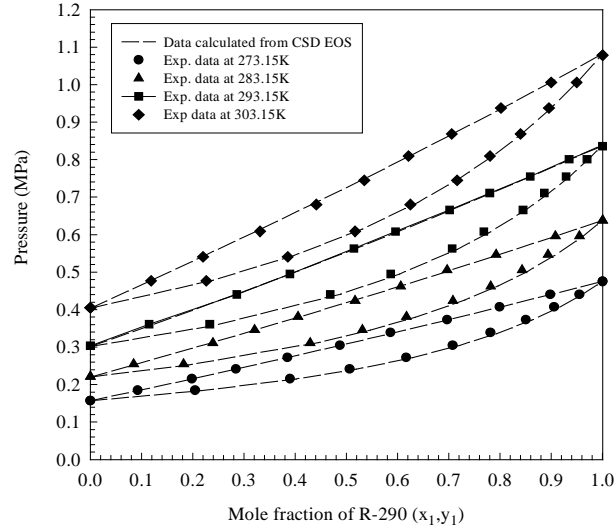
Table 2. Comparison of the vapor pressure (P_v) of pure components between experimental data and data obtained from the database REFPROP 6.01 [14]

Component	T (K)	$P_{v,\text{exp}}$ (MPa)	$P_{v,\text{REF}}$ (MPa)	$\Delta P_v/P_{v,\text{exp}}$ (%) ^(b)
R-290	273.15	0.4750	0.4743	0.15
	283.15	0.6378	0.6364	0.19
	293.15	0.8360	0.8362	0.02
	303.15	1.0784	1.0790	0.06
				Ave. 0.11
R-600a	273.15	0.1572	0.1564	0.51
	283.15	0.2218	0.2201	0.77
	293.15	0.3034	0.3018	0.53
	303.15	0.4052	0.4043	0.22
				Ave. 0.51

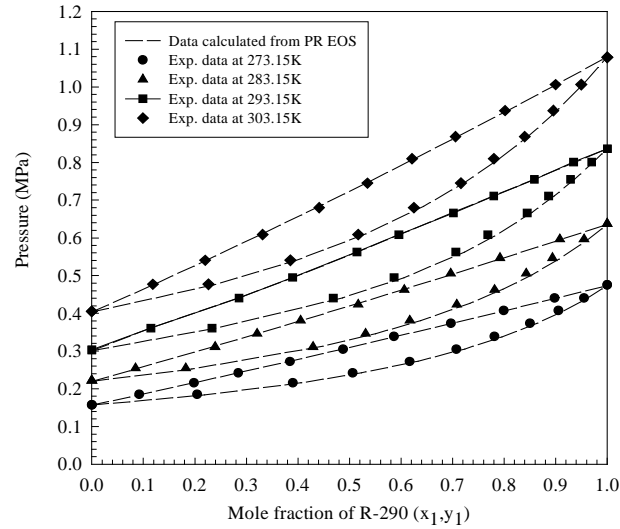
(b) $\Delta P_v = |P_{v,\text{exp}} - P_{v,\text{REF}}|$

The P-x-y diagram for the mixture R-290/R-600a at different temperatures are shown in Figure 2 where the experimental VLE data at 273.15, 283.15, 293.15, and 303.15 K are shown as closed circles, triangles, squares, and diamonds, respectively. The black dash lines represent the calculated data by CSD-EOS (Figure 2a) or by PR-EOS (Figure 2b). Both experimental and calculated P-x-y diagrams indicate that the azeotropic behavior was not found for this mixture in the temperature range from 273.15 to 303.15K and the calculated diagrams did not coincide accurately with corresponding experimental one. This difference can be demonstrated clearly by the deviations of vapor phase

composition and pressure of the calculated data compared with experimental one in each point, which are shown in Figure 3 and Figure 4.



(a) Experimental data and data calculated from CSD-EOS

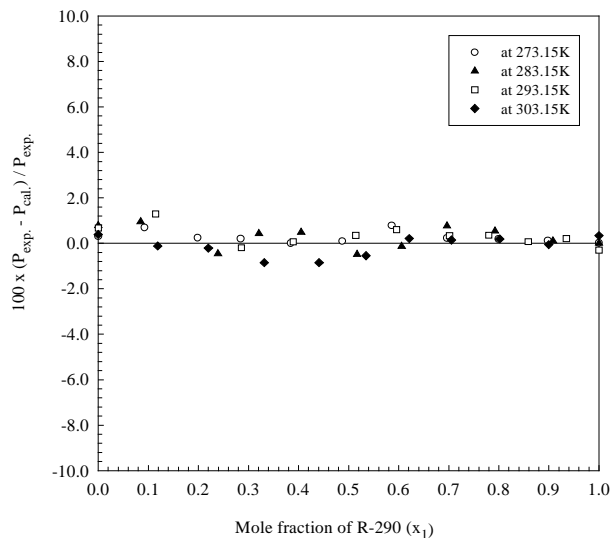


(b) Experimental data and data calculated from PR-EOS

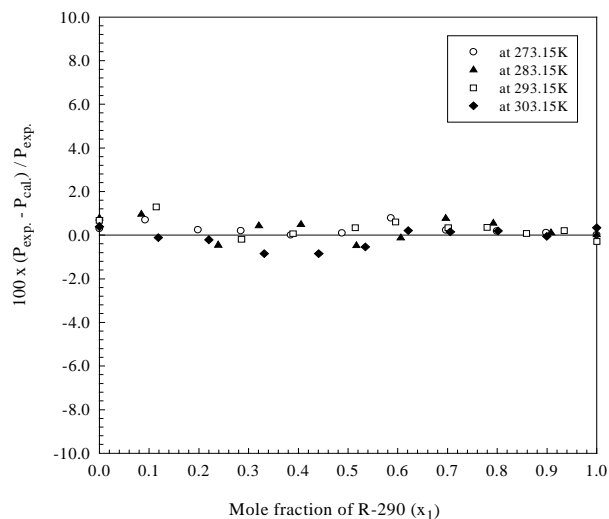
Figure 2. P-x-y diagram for the mixture R-290/R-600a at different temperatures

The interaction parameters and the average deviations of pressure (AD-P (%)) and average deviation of vapor phase composition (AD-y) between measured and calculated values for the mixture R-290/R-600a are reported in Table 3. It indicates that in the

temperature range from 273.15 to 303.15K, the values of AD-P(%) of data calculated by CSD-EOS and by PR-EOS varied within 0.26 ~ 0.47% and 0.29 ~ 0.53%, respectively. Also, the AD-y varied within 0.005 ~ 0.011 for CSD-EOS and 0.007 ~ 0.013 for PR-EOS. All values are relatively low and acceptable. In other way, the data calculated by using both of CSD-EOS or PR-EOS give a good agreement with the experimental data.

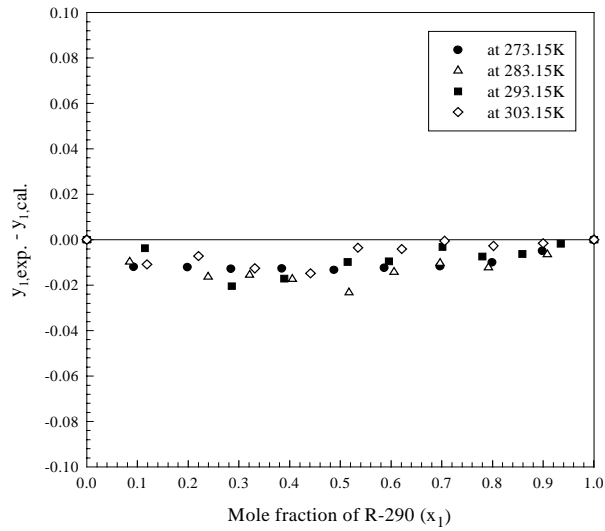


(a) Deviations of calculated pressures obtained from the CSD-EOS

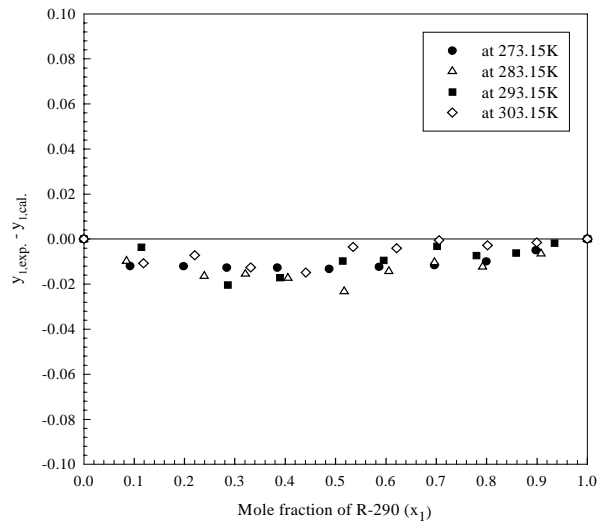


(b) Deviations of calculated pressures obtained from the PR-EOS

Figure 3. Deviations between experimental and calculated pressures for the mixture R-290/R-600a at different temperatures



(a) Deviation of calculated vapor phase compositions obtained from the CSD-EOS



(b) Deviation of calculated vapor phase compositions obtained from the PR-EOS

Figure 4. Deviations between experimental and calculated vapor phase compositions for the mixture R-290/R-600a at different temperatures

5. Conclusions

Measurements of the vapor-liquid equilibria for the mixture of R-290/R-600a at four equally spaced between 273.15 and 303.15K were carried out by using a circulation-type equilibrium apparatus. It was found that this mixture did not show azeotropic behavior in the range of temperature above.

The experimental VLE data were correlated with those data calculated by the CSD-EOS and the PR-EOS combined with the Wong-Sandler mixing rule. Good agreement

between experimental and calculated data strongly indicates that both of the CSD-EOS and PR-EOS can be used well to estimate the thermodynamic properties for the binary mixture R-290/R-600a in the range of temperatures between 273.15 and 303.15K and expectantly applied to other ranges but it needs some further experiments to confirm.

List of symbol

A_{∞}^E	An excess Helmholtz free energy
$a(a_{ij})$	equation of state attraction parameter (between species i and j)
$b(b_{ij})$	equation of state volume parameter (between species i and j)
b	a constant
C	a numerical constant equal to $\ln(\sqrt{2}-1)/\sqrt{2}$ for the PR-EOS
f_{12}, k_{12}	interaction parameter between species 1 and 2
g_{ij}	an interaction energy parameter of the i-j component
G_{ij}	the local composition factor for the NRTL model
P, P_c, P_v	pressure, critical pressure, vapor pressure (MPa)
R	gas constant, $R = 8.3144 \text{ (J mol}^{-1} \text{ K}^{-1})$
T, T_c	absolute temperature, critical temperature, (K)
T_r	reduced temperature
V, V_M	total volume, molar volume
x, y	mole fraction in liquid phase, in vapor phase
y	$b/4V_M$

Greek letters

$\alpha(T)$	temperature dependent
$\alpha_0, \alpha_1, \alpha_2$	coefficients for the temperature dependence of α
Δ, δ	change in a quantity
ω	acentric factor
ω_L	weighting factor for liquid volume
ω_P	weighting factor for saturation pressure
ω_v	weighting factor for vapor volume
ω_y	weighting factor for vapor phase composition

Subscripts

Ave.	average
c	critical property
cal	calculated
exp	experimental
i, j	$i^{\text{th}}, j^{\text{th}}$ component of the mixture
l,v	liquid, vapor phase
m	mixture

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